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EFFECT OF FIRING TEMPERATURE ON THE PROPERTIES OF SOL-GEL FILMS OF THE CuO – TiO₂ SYSTEM

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The viscosity, surface tension, and refractive index of 2-day-old film-forming solutions of the CuO – TiO₂ system of different composition were compared with the structure and properties of coatings on float glass made from them. Regardless of the composition and firing conditions, the film thickness remained constant. The refractive index and mirror reflection coefficient of the coatings are correlated by a directly proportional dependence. Increasing the firing temperature does not change or increases the values of the refractive index and mirror-reflection coefficient of the films. The chemical resistance of the coatings to water or hydrochloric acid solution is not a function of or improves with an increase in the firing temperature.

The properties of glass are related to the equilibrium diagram of the corresponding system to a significant degree and are a function of the thermal history [1], determined by the temperature-time conditions of melting, firing, and finishing of the glass. In [2], it is assumed that the nature of thin-layer sol-gel coatings is close to glass. This forms grounds for hypothesizing that their properties will definitely be a function of the conditions of thermal treatment (firing temperature and firing time) of the films.

We investigated the correlation between the thermal history and properties of films of different molar composition made from 2-day-old film-forming solutions (FFS).

We studied five compositions in the two-component CuO – TiO₂ system which differed in the ratio of the film-forming oxides or raw materials used for fabricating the FFS. Copper oxide was added to a solution with copper chloride or nitrate, TiO₂ was added with alkoxides: tetraethoxytitanium Ti(OC₂H₅)₄ (TET) or tetrabutoxytitanium Ti(OC₄H₉)₄ (TBT). Hydrochloric or nitric acid (if the copper oxide was added with chloride or nitrate, respectively) was the catalyst of hydrolysis of the alkoxides and ethyl alcohol was the solvent. The total mass content of film-forming oxides in all solutions (concentration of FFS) was the same and equal to 5%. The sol ripening time was 2 days. The viscosity of the FFS was measured by the capillary method (VPZh-1 viscometer) and the surface tension was measured by the sessile drop method.

Samples of thermally polished sheet glass measuring 70 × 70 × 5 mm were immersed in the solution and removed at the constant rate of 1 mm/sec, then held for 2–3 h in air

at room temperature to complete hydrolysis and polycondensation processes, and fired in a furnace with Silit heaters at 350, 450, or 550°C for 30 min. All measurements were performed on the side of the glass in contact with the protective gas atmosphere of the furnace during processing.

The structural changes in the films were investigated with micrographs made with magnification of 100 times (MIM-8M light microscope). The refractive index n , thickness h (LEF-ZM-1 ellipsometer), and mirror-reflection coefficient R (Pulsar spectrophotometer) were measured. The chemical stability T was estimated by the decrease in the thickness of the coating after etching in water (30 days) or 0.1 N HCl (30 min) [3]. According to the method used, the chemical stability will be higher the lower the value of T is.

All experiments and measurements were conducted repeatedly and the results were statistically processed. The structural-phase transitions that take place when the composition changes or the FFS ages were investigated by DTA and RPA of powders obtained by evaporating the corresponding solutions.

The molar content of copper and titanium oxides in the films and the results of XPA of powders are reported in Table 1 and Fig. 1 shows the results of DTA of powders made from FFS of different composition.

No chemical compounds were detected among the film-forming components in powders of all compositions. In going from composition No. 1 to composition No. 3, the amount of TiO₂ crystalline phase in the initial powders decreased, while the amount of CuCl₂ · 2H₂O increased, which corresponds to the content of these components in the FFS and films. We can hypothesize that the solubility of copper chloride in ethanol is low and when the solvent is eliminated,

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TABLE 1

Composition	Molar content in film, % (incorporation in FFS)		Results of XPA of powders obtained from 2-day-old FFS*	
	CuO	TiO ₂	initial	heated to 800°C
No. 1	15 (copper chloride)	85 (TBT)	73 TiO ₂ ** 33 CuCl ₂ · 2H ₂ O	240 TiO ₂ ***
No. 2	30 (copper chloride)	70 (TBT)	44 TiO ₂ ** 103 CuCl ₂ · 2H ₂ O	248 TiO ₂ *** 25 CuCl ₂ · 2H ₂ O
No. 3	45 (copper chloride)	55 (TBT)	43 TiO ₂ ** 220 CuCl ₂ · 2H ₂ O	185 TiO ₂ *** 45 CuCl ₂ · 2H ₂ O
No. 4	30 (copper nitrate)	70 (TBT)	65 TiO ₂ ** 101 Cu ₂ (OH) ₃ NO ₃	242 TiO ₂ ***
No. 5	30 (copper chloride)	70 (TET)	36 TiO ₂ ** 209 CuCl ₂ · 2H ₂ O	168 TiO ₂ *** 150 CuCl ₂ · 2H ₂ O

* The content is indicated in arbitrary units.

** TiO₂ primarily in the form of anatase.

*** TiO₂ primarily in the form of rutile.

TABLE 2

Composition	Properties of FFS*		
	refractive index	viscosity, mm ² /sec	surface tension, 10 ⁻³ N/m
No. 1	1.3919	3.21	23.0
No. 2	1.3895	2.92	26.5
No. 3	1.3878	2.74	25.2
No. 4	1.3892	2.87	24.3
No. 5	1.3849	2.96	28.7

* There was no sediment in all cases.

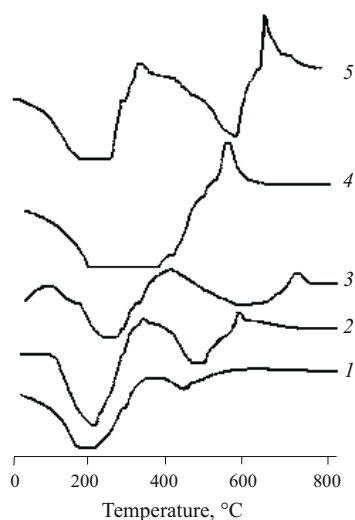
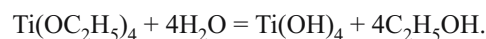


Fig. 1. Thermograms of powders obtained from 2-day-old FFS. The numbers of the curves correspond to the numbers of the compositions.

it crystallizes in the form of branched (dendritic) inclusions which are clearly seen in the films even at low magnification. The intensity of crystallization is proportional to the concentration of CuO in the coatings and CuCl₂ · 2H₂O in the corresponding powder.

A successive shift of the exothermic effects to the high-temperature region takes place simultaneously in the corresponding thermograms (see Fig. 1, curves 1 – 3). The same characteristics persist in general in the powders treated up to 800°C, while the amount of CuCl₂ · 2H₂O was less than in the initial powders due to decomposition of copper chloride. According to the data in [4], copper(II) chloride boils with decomposition at 993°C. The observed occurrence of this process in FFS powder at a much lower temperature (800°C) can probably be attributed to an increase in the dispersion of the particles to sizes comparable to molecular sizes.

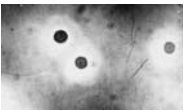
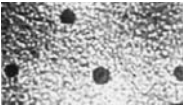
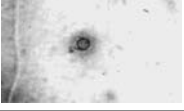
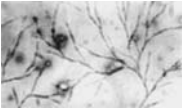








According to the XPA data, no reactions between CuO and TiO₂ were also found in powders Nos. 4 and 5. The TiO₂ phase was larger in initial powder No. 4 and smaller in powder No. 5 than in identical powder No. 2. Cu₂(OH)₃NO₃ crystals were presented in composition No. 4 and disappeared after thermal treatment at 800°C. According to the data in [5], the copper nitrate used as copper-containing raw material easily decomposes at a low temperature. The good solubility of this compound in ethanol [6] resulted in a film almost free of inclusions. The CuCl₂ · 2H₂O phase was larger in powder No. 5 than in powder No. 2, probably due to worsening of the solubility of copper chloride because of entry into the system of additional amounts of ethanol formed in hydrolysis of TET according to the reaction:



We note that butyl alcohol is separated in hydrolysis of TBT in compositions No. 1 – 4. There was a marked shift of the exo- and endothermic effects to the high-temperature region in the thermogram of powder No. 5 in comparison to powder No. 2 (see Fig. 1).

The properties of FFS of different composition and age are reported in Table 2. There were obviously no sediments in the 2-day-old FFS. The refractive index and viscosity of solutions No. 1 – 3 successively decreased, while the surface tension increased. The refractive index decreased due to a decrease in the proportion of TiO₂ in the coating and TBT in the FFS, hydrolyzed into highly refractive butyl alcohol ($n = 1.39931$; for comparison: ethanol has $n = 1.3611$ [6]). The decrease in the viscosity is due to the particle shape, since the viscosity of sols containing elongated particles will be smaller for the same volume proportion [7]. The increase in the surface tension is related to an increase in the specific surface area of the disperse phase in going from composition No. 1 with spherical particles to composition No. 3 with branched dendritic particles (Table 3).

TABLE 3

Composition	Firing temperature, °C	Confidence intervals of distribution of the properties of the coatings					Photomicrographs of the coatings (× 100)
		<i>n</i>	<i>R</i> , %	<i>T</i> _{H₂O} , %	<i>T</i> _{HCl} , %	<i>h</i> , Å	
No. 1	350	2.025 – 2.007	33.7 – 28.9	20.3 – 18.3	0	980 – 950	
	450	No data					
	550	2.124 – 2.104	37.9 – 37.6	No data		890 – 790	
No. 2	350	1.994 – 1.980	34.7 – 33.7	14.4 – 12.0	0	720 – 690	
	450	2.132 – 1.988	34.8 – 34.0	13.0 – 7.0	19.0 – 14.0	720 – 610	
	550	2.151 – 1.931	34.1 – 32.5	No data		790 – 700	
No. 3	350	1.942 – 1.896	30.1 – 27.5	41.4 – 34.2	17.0 – 5.8	790 – 650	
	450	2.083 – 1.826	33.7 – 29.1	23.0 – 5.0	23.0 – 7.0	920 – 570	
	550	1.907 – 1.835	29.9 – 26.8	22.5 – 5.3	22.7 – 6.5	730 – 590	
No. 4	350	1.884 – 1.720	21.6 – 17.8	32.9 – 25.9	20.2 – 13.8	1040 – 820	No data
	450	1.793 – 1.777	19.2 – 17.0	No data		830 – 780	
	550	1.848 – 1.804	20.8 – 18.4	23.6 – 5.5	25.9 – 5.1	960 – 720	No data
No. 5	350	1.989 – 1.913	35.3 – 33.9	34.1 – 25.9	14.8 – 10.0	660 – 530	
	450	2.019 – 1.895	34.6 – 32.7	27.4 – 9.0	28.1 – 9.1	580 – 340	
	550	1.961 – 1.881	39.0 – 38.6	No data		600 – 470	

Within the limits of the experimental error, the refractive indexes of FFS Nos. 2 and 4 are the same, while the viscosity and surface tension of FFS No. 4 is lower due to a decrease in the amount of dendritic particles in the solution and coating.

In comparison to FFS No. 2, the refractive index is lower for solution No. 5, probably due to enrichment of the sol with low-refractive ethyl alcohol formed in hydrolysis of TET, while the viscosity and surface tension are higher due to intensification of the "dendritic character" of the particles (see Table 3).

The firing temperature (duration of 30 min) and some properties of the coatings made from 2-day-old FFS are reported in Table 3.

In increasing order of the confidence intervals of the distribution of the values of n , R , h , T_{H_2O} and T_{HCl} , the coatings heat-treated at a fixed temperature can be arranged in the sequence (the figures in the sequences are the composition number):

350°C n : 1 = 2 > 3, 2 = 5, 2 > 4;
 R : 2 > 1 = 3, 2 = 5, 2 > 4;
 h : 1 > 2 = 3, 4 > 2, 2 > 5;
 T_{H_2O} : 3 > 1 > 2, 4 > 2, 5 > 2;

T_{HCl} : 3 > 1 = 2, 4 > 2, 5 > 2;
 450°C n : 2 = 3, 2 > 4, 2 = 5;
 R : 2 = 3, 2 > 4, 2 = 5;
 h : 3 > 2, 4 > 2, 2 > 5;
 T_{H_2O} : 2 = 3, 2 = 5;

T_{HCl} : 2 = 3, 2 = 5, 2 > 4;
 550°C n : 1 = 2 > 3, 2 = 5, 2 > 4;
 R : 1 > 2 > 3, 2 = 5, 2 > 4;
 h : 1 = 2 = 3, 2 = 4, 2 > 5;
 T_{H_2O} : insufficient data;

T_{HCl} : insufficient data.

In going from composition No. 1 to composition No. 3, the refractive index and mirror-reflection coefficient of the coatings decrease or do not change. In comparison to composition No. 2, the values of these parameters for film No. 5 remained constant, while they decreased for film No. 4. This could be due to the different effect of the initial copper nitrate and chloride on the structure and physical properties of the coatings. For this reason, one method of correcting the characteristics of sol-gel coatings is to rationally select the initial components for preparation of the FFS. We note that in traditional glass-making technology, the raw materials significantly affect the spectral characteristics while almost not altering the other properties.

The analysis of the sequences shows that as in glass, the refractive index and reflection coefficient of the coatings are directly proportionally correlated. The differences observed at 350°C for coatings Nos. 1 – 3 can be attributed to the error of measurement.

No distinct correlation was found between the thickness, chemical stability, and composition of the coatings.

A similar analysis of the properties of coatings of fixed composition treated with heat at a different temperature was conducted. The following were obtained as a result (figures in sequences — firing temperature):

No. 1 n : 550 > 350;
 R : 550 > 350;
 h : 550 < 350;
 T_{H_2O} : insufficient data;

T_{HCl} : insufficient data;

No. 2 n : 350 = 450 = 550;
 R : 350 = 450 = 550;
 h : 350 = 450 = 550;
 T_{H_2O} : 350 = 450;

T_{HCl} : 450 > 350;

No. 3 n : 350 = 450 = 550;
 R : 350 = 450 = 550;
 h : 350 = 450 = 550;
 T_{H_2O} : 350 > 450, 550;

T_{HCl} : 350 = 450 = 550;

No. 4 n : on the whole — 350 = 450 = 550, in particular — 550 > 450;
 R : 350 = 550 = 450;
 h : 350 = 550 ≥ 450;
 T_{H_2O} : 350 > 550;

T_{HCl} : on the whole — 350 = 450 = 550, in particular — 350 > 450;

No. 5 n : 350 = 450 = 550;
 R : 550 > 350, 450;
 h : 350 = 450 = 550;
 T_{H_2O} : 350 = 450;

T_{HCl} : 350, 450 > 550.

As a result of analyzing the sequences, it was found that the refractive index of the coatings is not a function of or increases with an increase in the temperature. This is due to the systematic decrease in the porosity of the films, which significantly affects the refractive index n_{eff} of a porous body according to the equation [8]:

$$n_{\text{eff}} = n_1 - \text{Po}(n_1 - n_3) - (n_2 - n_3)f(P/P_0),$$

where n_1 , n_2 , and n_3 are the refractive indexes of the substance constituting the skeleton of the layer, the adsorbed water, and air; Po is the porosity; $f(P/P_0)$ is the equation for the adsorption isotherm written in general form.

The reflection coefficient increases with an increase in the firing temperature for compositions Nos. 1 and 5 and is not a function of the temperature for compositions Nos. 2 – 4.

The thermal treatment conditions do not markedly affect the thickness of the films. Within the limits of the experimental error, the coatings are not sensitive to the effect of water and the hydrochloric acid solution in 50% of the cases,

and the chemical stability improves with an increase in the treatment temperature in the other cases. This is due to a decrease in the porosity of the coatings and difficulty in penetration of the etching agent into the depths of the film.

A correlation was thus found between the parameters of the FFS, the XPA results, and the structure formed in the coatings in the CuO – TiO₂ film-forming system. The properties of FFS and the investigated coatings are sensitive to the nature of the initial components used to prepare the sols. Regardless of the compositions and firing conditions of the films, their thickness remains constant. The refractive index and mirror-reflection coefficient of coatings of the CuO – TiO₂ system are correlated by a directly proportional dependence.

Increasing the treatment temperature does not alter or increases the value of the refractive index and mirror-reflection coefficient of the films. Their chemical stability in exposure to water or hydrochloric acid solution is not a function of or improves with an increase in the firing temperature.

REFERENCES

1. L. I. Demkina, *Physicochemical Methods in Production of Optical Glass* [in Russian], Khimiya, Leningrad (1976).
2. N. V. Suikovskaya, *Chemical Methods of Manufacturing Thin Transparent Films* [in Russian], Khimiya, Leningrad (1971).
3. A. B. Atkarskaya, V. I. Borul'ko, and S. A. Popovich, "Effect of aging the solution on the properties of films of the CuO – TiO₂ system," *Steklo Keram.*, No. 10, 15 – 18 (1995).
4. *Handbook of Chemistry* [Russian translation], Khimiya, Leningrad (1975).
5. N. L. Glinka, *General Chemistry* [in Russian], Integral-press, Moscow (2004).
6. V. A. Rabinovich and Z. Ya. Khavin, *Short Chemical Handbook* [in Russian], Khimiya, Leningrad (1978).
7. N. S. Voyutskii, *Course in Colloid Chemistry* [in Russian], Khimiya, Moscow (1964).
8. P. G. Cheremskoi, V. V. Slezov, and V. I. Betekhtin, *Pores in Solids* [in Russian], Énergoatomizdat, Moscow (1990).